APPENDIX C TO NELAC STANDARDS CHAPTER 5
Laboratory Measurement System Evaluation Protocol

C.1 Purpose:

This Appendix serves to assess whether or not a particular measurement system is suitable for an intended purpose. It also defines the documentation necessary to provide evidence that a method was appropriately evaluated.

Note: The activities specified in this appendix are not suitable for demonstrating that a method, when considered independent of a laboratory's quality system, is valid. That activity generally requires a collaborative study such as is described in ASTM D-2777.

C.2 Background:

The bases for evaluating whether a measurement system's performance is suitable for a particular purpose are Measurement Quality Objectives (MQOs). MQOs include sensitivity and range, precision, bias, and selectivity. The measurement system is a method as implemented at a particular laboratory (i.e., the laboratory SOP, equipment and staff).

A measurement system is suitable for its intended purpose if its performance meets the requirements that have been established for the purpose at hand. Thus a measurement system may be suitable for one purpose but not be appropriate for a different application. The criteria for suitability are the MQOs. The bias, precision and sensitivity characteristics determined for the measurement system are compared to the MQOs. If the laboratory determined bias, precision and sensitivity, defined in this appendix as measurement quality characteristics (MQCs) do not meet the respective MQOs, then the measurement system does not yield data suitable for its intended purpose. The selectivity of the measurement system is evaluated as part of the bias evaluation. In addition, appropriate selectivity checks should be established within the method, including mass spectral tuning, second column confirmation and related activities.

The measurement system evaluation process for a laboratory is twofold. An Initial Measurement System Evaluation, the focus of this appendix, is done when the laboratory implements a method for the first time, or significantly modifies a method that has previously been evaluated by the laboratory and is performed to demonstrate that the laboratory and method (the measurement system) is capable of providing data of the quality needed. The activities required for this evaluation are summarized in Table C-1. An Ongoing Measurement System Evaluation is done as a part of routine operations to document the performance of the method on actual samples. Specifics of the Ongoing Evaluation are covered in Appendix D.

The role of the laboratory includes:

Evaluate client MQOs and specific method requirements, if any, to assist in the method selection process.

Perform Initial Evaluation of test methods and measurement systems to determine the associated Method Quality Characteristics (MQCs).

Perform Ongoing Evaluation of test methods and measurement systems to determine the associated measurement quality characteristics in light of specific Method Quality Objectives specified by the client; report the sample results together with the measurement quality characteristics to the client.

Report MQCs determined together with sample results if the client does not specify MQOs.

Employ test procedures that meet the needs of the client.

C.3 Initial Measurement System Evaluation - General

The initial evaluation must be performed even if the laboratory uses a published standardized method with no modifications; it demonstrates the laboratory's ability to use this method correctly. Sample specific modifications (i.e., using a smaller sample size; adding a cleanup step) can be performed without re-doing the method evaluation as long as the changes can be scientifically justified as not being ones that would change the nature of the procedure and the appropriate ongoing quality control sample analyses are used to document the measurement system performance, and the changes, the rationale for the changes not having to be evaluated using the initial evaluation procedure are contained in the documentation (e.g., case narrative, corrective action form, non-conformance memo) of the analysis.

When a new analyte is added to an existing method, an initial method evaluation must be performed for that analyte unless the laboratory can demonstrate, by the nature of the analyte being added, that all measures of system performance can be assured (e.g., isomer of previously evaluated constituent that does not exhibit chromatographic interference with other target analytes).

C.4 Incorporation of MQOs

When MQOs are not provided to the laboratory, the laboratory may use the performance characteristics of published standardized methods as MQOs, or may establish MQOs based on the MQC data obtained from an initial evaluation. When laboratory clients provide the laboratory with the required MQOs, the laboratory shall compare these MQOs to the performance of the measurement system as determined in an initial evaluation or with limited development from periodic review of on-going performance evaluations. If the measurement system performance is not adequate (i.e., does not meet one or more of the MQO requirements) for the intended purpose, the laboratory must notify the client; if the method is modified to achieve improved MQOs, the

initial evaluation must be repeated.

C.5 Matrices and Sample-Types

The activities described below for an initial method evaluation must be performed for every method in the laboratory and for every sample-type to which the method is applied. The sample-types described below refer to a sample with certain properties within the broadly defined NELAC matrices, (Drinking Water; Non-Potable Water; Solid and Chemical Materials; Biological Tissues; and Air and Emissions)that provides a reasonable challenge to the method, but that does not address all potential matrix issues that could exist in actual samples. If the method is to be used on sample matrices which provide a more significant analytical challenge (e.g., sludges, chemical wastes, oils, brines), the on-going method evaluation activities must be used to document the performance of the method in these other matrices. Alternatively, the laboratory may perform an initial evaluation on these samples. Laboratories have the option to perform the initial evaluation on samples collected from a specific site (e.g., a POTW can use the wastewater discharged from their facility) provided the method is only used to analyze those samples or samples with comparable characteristics.

The sample-type for the Drinking Water matrix is tap water from the laboratory.

The Non-Potable Water sample type shall have the following characteristics:

Total suspended solids (TSS) greater than 40 mg/L
Total dissolved solids (TDS) greater than 100 mg/L
Soluble organic content greater than 20 mg/L
Salt content greater than 120 mg/L
Total Alkalinity greater than 140 mg/L

If the initial method evaluation is performed on a Non-Potable Water sample-type, then the method may be applied to all Drinking Water and Non-Potable Water samples. However, if the initial evaluation is performed on a Drinking Water sample-type, the method may be applied to other sample-types within the Drinking Water matrix only.

For the Solid and Chemical Materials matrix the appropriate sample-type is a soil or sediment containing at least 10% each of sand, silt and clay and at least 5% moisture.

Within the Biological Tissues matrix the appropriate sample type is any fish or animal tissue that contains at least 5% fat.

Within the Air and Emissions matrix separate initial evaluations are required for canister or other whole-volume air samples, Polyurethane foam plugs (PUF) samples, filter media or the various absorption tube media.

C.6 Evaluation of Sensitivity:

C.6.1 Detection Limit:

When required by a regulation or the client, the Detection Limit shall be established for every analyte in each sample-type for which data are to be reported. If an agency or program requirement is in place, it shall be followed. In other instances any procedure for establishing the Detection Limit which exists in EPA regulations or guidance or in the peer-reviewed literature, may be used. When clients request data be reported to detection limits, then the validity of the detection limit determination is demonstrated by qualitative identification of the analyte in a clean sample of the matrix.

Detection limits must be determined each time there is a change in the test protocol that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis.

All sample processing steps of the analytical protocol shall be included in the determination of the detection limit. Instrument detection limits are not acceptable substitutes for the above referenced determinations.

All procedures used must be documented. Documentation must include the sample-type. All supporting data must be retained.

A detection limit study is not required for any component or property for which spiking solutions or quality control samples are not available.

C.6.2 Quantitation Limit:

The minimum level of quantitation shall be established for every analyte for which quantitative data are to be reported. The minimum level of quantitation is the lowest value for which unqualified quantitative data may be reported by the laboratory. When determining the quantitation limit, if client, regulatory agency, or other requirements are in place, those requirements shall be followed. In other instances, any procedure for establishing the quantitation limit may be used as long as the validity of the determination is confirmed by successful analysis of triplicate clean samples of the matrix spiked with the analytes of concern at the claimed quantiation limit. A successful analysis is one where the mean recovery of each analyte is within the established MQOs for bias and the variability of the triplicate measurements meets the MQO standard for measurement system precision.

Note: The Quantitation limit may not be lower than the level of the lowest calibration standard.

Demonstration of the QL is to be performed by analyzing a spiked matrix type containing each analyte in triplicate at a concentration at or near the QL. The mean recovery for each analyte must be within the established MQOs for bias and precision. If no MQO's exist, the laboratory determined

MQCs are established from the data generated in this verification.

If project-specific MQOs have quantitation limit requirements greater than the QL, the laboratory may analyze triplicate samples at the lowest concentration of concern, unless the laboratory prefers to demonstrate performance at a lower concentration, or has existing data that documents that the required sensitivity can be achieved.

All sample processing steps of the analytical protocol shall be included in the determination of the quantitation limit.

All procedures used must be documented. Documentation must include the sample-type. All supporting data must be retained.

A quantitation limit study is not required for any component or property for which spiking solutions or quality control samples are not available.

C.7 Determination of Bias, Range and Precision

If sample results are to be reported over a concentration range, the study described below must be performed. If the objective of the sample analyses is to demonstrate the presence or absence of an analyte at a specific concentration, or to establish whether or not the concentration is above or below a specified value, then this determination need not be performed as the triplicate analyses required above for the quantitation limit are adequate.

Fortify each matrix type in triplicate at or near the quantitation limit, at the upper-range of the calibration (upper 20%), and fortify each matrix in quadruplicate at a mid-range concentration. If a Certified Reference Material (CRM) of the same matrix type as the samples is available, substitute the CRM for the mid-range replicates. Process these samples as a three sets of samples through the entire measurement system for each analyte of interest. For projects that will span more than 3 days of analytical work, each set, containing the concentration range of interest, should be processed (including sample preparation steps) and analyzed on separate days. (This means that each day one sample at each concentration is analyzed.) The fourth sample at the mid-range concentration can be included on any of the 3 days. A separate method blank shall be subjected to the analytical method along with the fortified analytes on each of the three days. (Note that the three samples at the QL concentration demonstrate sensitivity as well.) For each analyte, calculate the mean recovery for each day, for each level over days, and for all ten samples. Calculate the relative standard deviation for each of the separate means obtained.

Compare the results at each concentration to see if there is a significant difference in either bias or precision as a function of concentration. If there is no significant difference, calculate the mean recovery and standard deviation over the range of interest by combining all values. If there is a

significant difference, calculate the mean recovery and standard deviation at each concentration. Evaluate the blank data for an indication of a positive bias. Compare these calculated results to the MQOs and determine if the method is adequate for its intended use. If no MQO's exist the laboratory uses these data to establish the MQCs.

C.8 Selectivity

The minimum requirement is to ensure that the measurement system is adequately selective. This includes performing the appropriate instrument set-up and performance checks (e.g., ICP interelement interference checks, MS tune, determination of chromatography retention time windows).

Confirmation shall be performed to verify the compound identification when positive results are detected on a sample from a location that has not been previously tested by the laboratory, or any positive results must be noted as unconfirmed. Such confirmations shall be performed on both elemental and organic analytes or when recommended by the test method. Confirmation is required unless stipulated in writing by the client. All confirmations shall be documented.